

phalanx of the great toe, arising fleshy from the tibia, inside the *extensor proprius*, and below the *tibialis anticus*. Strong tendon implanted into base of first phalanx inside the short common extensor.

30. The same muscle in another subject, having a different arrangement. Arising from the interosseous ligament *outside* the *extensor proprius*, and inserted by a tendon into that of the short common extensor going to the great toe. Neither of these have been before recorded.

31. A. The *deep flexor* tendon of the little toe supplied by a distinct muscle arising from the inner tubercle of the os calcis. Not before recorded.

B. A very large development of the *flexor accessorius* inserted into both the *long common flexor* and *long flexor of the great toe* tendons.

32. A. *Abductor ossis metatarsi quinti*.—A distinct muscle found by the author in more than one-half of the subjects in which he has looked for it, concealed by the outer part of the plantar fascia and *abductor minimi digiti* muscle, arising from the outer tubercle of the os calcis by a round fleshy belly, and inserted into the base of the fifth metatarsal by a distinct round tendon. Not before observed in the human subject. Found in the Gorilla and Chimpanzee by Huxley and Flower.

B. *Opponens minimi digiti*.—Very commonly found, though not described in anatomical text-books. Arises tendinous from the ligament of the fifth metatarsal and cuboid, and inserted in a bipennate way into the whole length of the fifth metatarsal bone. Found well developed in all the Apes.

IV. "Researches on Isomeric Alkaloids." By C. GREVILLE WILLIAMS, F.R.S. Received May 12, 1864.

(Abstract.)

The experiments recorded in the following paper have for their object the determination of two questions:—

1. Whether the base produced by destructive distillation of cinchonine, and having the formula $C^7H^{9'''}N$, is isomeric or identical with the lutidine from Dippel's oil? and

2. How far the chinoline series of bases, isomeric with the leukoline series, extends beyond lepidine?

In one form or another the observations have been going on for some years, but it is only lately that results have been obtained which appear conclusive.

The first of the above questions is connected with one of the most difficult problems occupying the attention of chemists at the present day, namely that of isomerism. It is true that some isomeric bodies differ so widely in their physical and chemical characters that no difficulty exists in distinguishing them. Thus the members of the aniline and pyridine series have, save their formulæ, few points of resemblance; cespitine and

amylamine could scarcely be confounded with each other. On the other hand, the two modifications of tartaric acid resemble each other so closely in their chemical characters, that it is chiefly by the observation of physical differences that they have been shown to be distinct.

The most difficult cases to solve are where the substances to be studied are so inert as to allow of few reactions by which they may be tested and compared. Thus, up to the present time, no crucial test has been devised by which the alcohol radicals can be distinguished from the isomeric hydrocarbons of Boghead naphtha and American petroleum; and, indeed, a change in opinion appears to be gaining ground, and the possibility of their being identical seems again to be entertained by at least one chemist who has carefully studied the subject*.

Another and scarcely less difficult case presents itself where a substance is supposed to be isomeric with another which at the time has no existence. Thus the constituent of oil of rue, long regarded as capric aldehyde, $C^{10}H^{20}O$ †, and which was subsequently shown to have the formula $C^{11}H^{22}O$ ‡, is by some chemists §, who do not dispute the accuracy of the latter formula, regarded as a ketone isomeric with the aldehyde of euodic alcohol. But if the substance from rue oil be not the aldehyde, then the real one is unknown, and consequently no means exist for a comparative study. The question is, in this instance, complicated by recent researches indicating ketones to be the aldehydes of alcohols formed by the hydration of olefants ||.

It is evident that the chances of isomeric bodies being formed in reactions, increase with the complexity of the type from which they are derived; or, in other words, the more replaceable hydrogen exists in the type, the greater the chances of isomerism in the derivatives. The ammonium and ammonia types always, therefore, present the greatest number of instances of isomerism.

In the course of the study of the organic bases produced by destructive distillation, the author very carefully compared the reaction of alkaloids from different sources, and he states that he was almost convinced of there being a true chemical difference between the chinoline and leukoline series before he succeeded in obtaining the decisive reaction resulting in the formation of the blue iodides from the amyl compounds of chinoline and lepidine. That observation led to the following comparative examination of the pyridine series as obtained from cinchonine with the corresponding series from Dippel's-oil and coal naphtha.

In order to submit the alkaloids to a searching examination, it was necessary that they should be in an equally high state of purity, and undergo the same amount of fractionation. The methods of preparation and

* Schorlemmer, Chem. Soc. Journ., xvi. p. 428.

† Gerhardt, Ann. de Chim. et de Phys. [3] xxiv. p. 103.

‡ C. G. W. Phil. Trans. 1858, p. 199.

§ Hallwachs, Ann. Pharm. cxiii. p. 107.

|| Berthelot, Comptes Rendus, lvii. 797, 63.

fractionation having, however, been described in his previous papers, the author does not further enter into them.

In a previous investigation it was found that in fractionating the bases from cinchonine, there was a tendency in the fractions boiling below chinoline to accumulate in larger quantities between 160° and 166° C.; and it was found on analysis that the distillate at that point had exactly the percentage composition of lutidine. The results of the analysis of the base and the platinum-salt pointed unmistakeably to the formula



The boiling-point of lutidine, according to Dr. Anderson, is 154° ; and it would therefore appear as if the base from cinchonine had a slightly higher boiling-point, but the author states that he does not draw any inference from that or any other isolated fact.

Physical Properties of the Bases.—Both bases, when pure, are colourless refractive oils, lutidine having a density of 0.9467 at 0° , and the cinchonine base (which the author distinguishes by the name of β -lutidine) of 0.9555 at the same temperature. Lutidine boils at 154° , β -lutidine between 163° and 168° .

Lutidine dissolves readily on shaking in three or four times its bulk of water; and, on warming, the liquid immediately becomes milky, and the base separates. β -lutidine, on the contrary, requires not less than twenty-five parts of water for solution, and does not present any signs of the very characteristic reaction of lutidine on warming the solution; on the contrary, a mixture of water and β -lutidine, cloudy from excess of base, clears on warming.

Lutidine has a most characteristic smell, resembling that of its lower homologues, but less pungent, and more approaching to aromatic. This smell is never altered in the least by any methods of purification. After boiling with nitric, chromic, or any other acid, the organic smell is given off on neutralization with an alkali. All its salts, however purified, have the same smell on the addition of an alkali.

β -lutidine has also a most characteristic smell, having not the faintest resemblance to that of lutidine. It cannot well be described, but, if anything, reminds one of nicotine; but it is without the peculiar pungency of that base. It is also far more pleasant. No treatment with acids or oxidizing reagents, and no amount of purification of its salt, causes the least alteration in the smell, or makes it approach, however distantly, to that of lutidine.

The vapour-density of lutidine, boiling at 154° , was determined by Dr. Anderson at 201° , and found to be 3.839.

The vapour-density of β -lutidine, boiling between 163° and 168° , was determined, for the purpose of this investigation, at 213° , and found to be 3.787. Theory requires 3.699.

From these numbers some important inferences may be drawn. It will be seen that the vapour-density, by experiment, is lower in the case of β -lutidine than in that of lutidine, although the former has a higher boil-

ing-point. It may be inferred from this that the boiling-point of β -lutidine has not been estimated above the truth, because if the fraction had been taken too high, the vapour-density would have erred considerably in excess. This will be the more evident if we consider that a determination of a vapour-density by the method of Dumas is, in fact, a process of fractional distillation; and if any base of higher formula had been mixed with it, it would have remained in the balloon, and increased the density to an extent proportional to the amount of impurity. The experiment, therefore, tends to show that the true boiling-point of lutidine is, if anything, a little below 154° , and that of β -lutidine is about 165° , inasmuch as the error is not greater than that usually observed with the purest substances obtained by fractional distillation.

The author, after stating that the specimen of lutidine employed in the investigation was prepared by Anderson himself, shows that lutidine retains its colourless state after rectification longer than β -lutidine.

Comparative Study of the Platinum-Salts of Lutidine and β -Lutidine.

The author states that before entering on the comparative examination of the bases, he determined their composition by converting them into platinum-salts. They both gave numbers so closely agreeing with those demanded by calculation from their formulæ, that it was evident that the specimens used were pure.

He then proceeded to ascertain whether any differences existed in their capability of yielding crystalline platinum-salts.

I. *β -Lutidine.*—A solution of hydrochlorate of the base was mixed with a solution of dichloride of platinum, the exact strength of the solutions being known. The mixture solidified instantly to a mass of crystalline plates. After 48 hours' repose their weight was determined and found to be 1.780 gramme.

II. *Lutidine.*—A precisely similar experiment was made with lutidine. No signs of crystallization appeared for 15 minutes. A few crystalline points then began to form. After 48 hours the weight of the crystals which had then formed was found to be 0.816 gramme.

The experiment was then repeated, a known weight of water being added to each solution.

III. *β -Lutidine.*—A large quantity of crystalline plates was deposited instantly. In five minutes the whole had solidified. After 48 hours' repose, the weight of the crystals was found to be 1.66 gramme.

IV. *Lutidine.*—No crystals appeared for 35 minutes. After 48 hours the weight of crystals formed was found to be 0.83 gramme.

The experiments III. and IV., like I. and II., show that β -lutidine, under exactly the same conditions, gives twice as much salt as the Dippel base.

As, according to Dr. Anderson, the presence of hydrochloric acid in excess greatly retards the formation of the lutidine salt, the author made

an experiment to ascertain if the retardation was equal in the case of β -lutidine.

V. β -*Lutidine*.—A mixture, the exact strength of which is given in the paper, containing a large excess of acid, was made. The whole instantly became nearly solid, and in five minutes the beaker could be inverted without any of the solid contents escaping. After twelve hours the weight of crystals formed was 1.70 gramme.

VI. *Lutidine*.—A precisely similar experiment was made with this base. No crystals appeared for thirty minutes. In twelve hours only 0.68 gramme had formed.

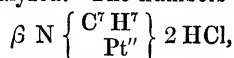
From the above experiments, it is evident that there is a vast difference in the tendency of the two bases to form crystalline platinum-salts.

Comparative Experiments upon the Decomposition by boiling of the Platinum-Salts of β -Lutidine and Lutidine.

The author describes in his paper the nature of the apparatus, and the precautions taken to ensure precision in the experiments.

I. β -*Lutidine*.—The salt begins to decompose the instant the solution enters into ebullition, an insoluble powder beginning to deposit. After forty minutes the operation had to be stopped, owing to the large quantity of insoluble sulphur-yellow precipitate which had fallen and rendered the boiling convulsive.

The salt formed in this manner was boiled with a fresh quantity of distilled water, and then analyzed. The numbers agreed with the formula

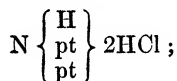


which is that of the bihydrochlorate of platino-lutidine, if regarded as analogous to the so-called bihydrochlorate of platinamine.

II. *Lutidine*.—The solution of the salt required two hours and a half of active boiling before even a trace of the insoluble precipitate began to form. After several hours more boiling, the deposit was excessively small. The author states that the difference in the behaviour of the two salts was so great, that it would be easy at any time to distinguish the two platinum-salts by this test alone.

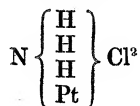
Platinum Compound of β -Lutidine isomeric with the Bihydrochlorate of Platino- β -Lutidine.

The author states his opinion that Gerhardt's theory of the platinum bases will require some modification to enable it to be applied to the analogous bodies obtained from the tertiary monamines. The bihydrochlorate of platinamine, the empirical formula of which is $\text{NH}^3, \text{Pt Cl}^2$, according to Gerhardt is constituted thus:—



but the author concludes that this formula is unsuitable to nitrile bases,

which contain no hydrogen capable of replacement by metals or organic radicals. Even assuming platinum in the above instance to be diatomic, there is no reason to suppose that the hydrogen driven out by the platinum has united to the chlorine to form two atoms of hydrochloric acid. The author then endeavours to show that the formula



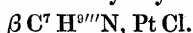
would in some respects be preferable, in which case the formula for the bihydrochlorate of platino- β -lutidine would become



He states, however, that a formula in which protochloride of platinum is made to replace one atom of hydrogen, would probably more nearly represent the constitution of the substance.

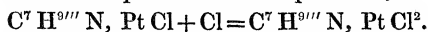
While studying these compounds, the author endeavoured to ascertain if compounds having the same composition as the so-called bihydrochlorates could not be formed by direct combination of the base with dichloride of platinum, instead of removing an equivalent of hydrochloric acid from the platinum-salt.

Dry dichloride of platinum, on being treated with excess of β -lutidine, evolved heat, and yielded an oily fluid, which solidified on cooling. After purification by treatment with dilute hydrochloric acid, a pale-brown amorphous powder resulted, which on analysis yielded the formula



From its totally different appearance, the author concludes that it is isomeric and not identical with the sulphur-yellow body produced by boiling the platinum-salt.

A third compound, isomeric or identical with one of the last-described bodies, should be produced by treating with chlorine the compound of lutidine, or β -lutidine with protochloride of platinum,



It is evident, even if the existence of bihydrochlorates of these platinum bases should ever be demonstrated, that *all* the compounds having the empirical relation $C^7 H^9 N, Pt Cl^2$ cannot be supposed to be constituted like Gerhardt's bihydrochlorate of platinamine. In fact, if we suppose that the product of the action of boiling water upon a platinum-salt yields such a substance, we must make the following admissions:—

1. That an atom of platinum or platinosum (Pt), under the form of two atoms of platinumum (pt²), may replace two atoms of hydrogen.

2. That a salt containing one atom of platinosum, with the equivalent 99, may, by boiling, become converted into a salt containing two atoms of platinumum with an equivalent 49.5.

3. That a salt containing a highly soluble compound with one equivalent of hydrochloric acid and two of chlorine, may, by loss of hydrochloric acid, become converted into an insoluble bihydrochlorate.

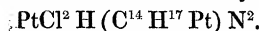
The author states his intention of studying more in detail the substances produced by the union of the primary and tertiary monamines with the chloride and dichloride of platinum, especially with the view of determining the amount of replaceable hydrogen in them.

Comparative Experiments on the Action of Protochloride of Platinum on β -Lutidine and Lutidine.

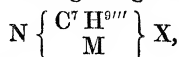
I. β -Lutidine.—Equal weights of protochloride and base were mixed in an apparatus surrounded with a non-conducting medium. The temperature rose from 16° to 84° , only one gramme of each ingredient being employed. The hard brittle product gave on analysis numbers almost exactly agreeing with the formula



According to Gerhardt's views the formula being doubled becomes the chloroplatinate of di-platoso- β -lutidine, and may be written thus:—

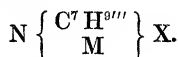


M. Hugo Schiff has recently presented to the Academy of Sciences* a paper in which he states that chinoline combines with numerous metallic chlorides to form compounds having the general formula



X representing an acid radical.

It is evident that this formula satisfies the condition of the compound above described containing β -lutidine. Representing the chlorine by X and the platinum by M, we have



But all these bodies are precisely analogous to the compound of chinoline with protochloride of platinum obtained by the author in the course of his researches on that base†.

II. *Lutidine*. When lutidine was treated with protochloride of platinum under exactly the same conditions, the temperature rose two degrees higher. The difference was therefore too small to found any conclusion upon. But the product, instead of becoming a hard brittle mass, remained of the consistence of treacle.

Comparative Examination of the Palladium Salts of β -Lutidine and Lutidine.

I. β -Lutidine.—A mixture of known quantities of base, hydrochloric acid, and chloride of palladium was made and put aside. In four days the whole was a nearly solid mass of garnet-red prisms. Collected and dried,

* Comptes Rendus, lvii. p. 837.

† Chemical Gazette, September 15, 1858.

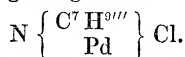
they weighed 816 milligrammes. On analysis they yielded numbers agreeing with the formula



Exposed for a long time to a heat of 100° , they become decomposed, one equivalent of hydrochloric acid being expelled from two equivalents of the salt. This was proved by analysis of the substance after leaving for five days, until in fact its weight became constant. The numbers obtained agreed with the formula



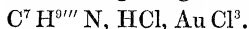
Chloride of Palladio- β -lutidyl Ammonium.—The author has succeeded in isolating the palladium base existing in the last substance. It is easily procured by acting on chloride of palladium in solution with β -lutidine. It is not readily soluble, and therefore precipitates at once. On analysis it gave numbers almost exactly agreeing with the formula



II. *Lutidine.* An exactly similar mixture of hydrochlorate of lutidine and chloride of palladium was made to the one in which β -lutidine was employed. No crystals, however, were obtained by the time that the contents of the vessel containing the β -lutidine had nearly solidified. After a month's repose, only 232 milligrammes had formed, instead of 816, as in the other experiment.

Comparative Experiments on β -Lutidine and Lutidine with Trichloride of Gold.

I. *β -Lutidine.*—A mixture of the hydrochlorate of the base and solution of trichloride of gold became nearly solid. On heating, a portion dissolved, and on filtration and cooling, gave a beautifully crystalline salt *a*. A large portion, however, melted to a dark oil, which dissolved in boiling dilute hydrochloric acid. On cooling, the salt was deposited in crystals *b*. Both portions on analysis gave numbers agreeing with the formula



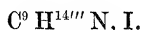
II. *Lutidine.*—A similar experiment was made. The precipitate only occupied half the bulk of the liquid; it did not require one-fourth part of the quantity of water to dissolve it that was necessary in the case of the β -lutidine.

The author in his paper gives the results of experiments made with the five bases and solution of trichloride of gold. The differences are fully as great as those observed with the hydrochlorates.

Action of Iodide of Ethyl on β -Lutidine and Lutidine.

I. *β -Lutidine.*—One volume of the base was mixed with two volumes of iodide of ethyl. The mixture was heated in a sealed tube for three minutes to a temperature of 94° . On removing the tube from the water-

bath in which it had been immersed, and plunging it in cold water, the whole solidified at once to a mass of crystals. On analysis, they gave results agreeing with the formula



II. *Lutidine*.—A mixture in similar proportions was heated to the same temperature for the same time. On cooling, it showed no signs of crystallization. It required an hour's digestion at 100° to effect combination. Even then no crystals were obtained on cooling. In twenty-four hours one-half of the product had crystallized. The rest remained in the form of a syrup.

Platinum-Salt of Ethyl β -Lutidine.

This salt was obtained from the iodide in the usual manner. It crystallizes in superb orange-coloured fronds. On analysis it yielded numbers pointing to the formula

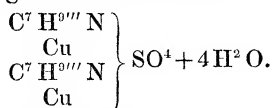


This salt, when boiled, undergoes a totally different decomposition from that afforded by the tertiary monamines under the same circumstances. The mixture turns black, and deposits the platinum. After two days' boiling, it yielded 27.5 per cent. of metal. The original salt contained 28.99.

Experiments were also made with the bases and solution of uranium. The results need not be quoted, as they merely confirm the previous ones, and show differences of the same character.

Compound of β -Lutidine with Sulphate of Copper.

When β -lutidine is gradually added to a solution of sulphate of copper, a copious pale green precipitate is formed. It dissolves in excess, forming a rich blue fluid. A small quantity of a pale green residue remains undissolved. The filtered solution soon becomes filled with brilliant blue prisms of considerable size. The air-dried salt retains four equivalents of water. On analysis the results agreed with the formula



Dried at 100° it loses two atoms of water, and at 200° it becomes anhydrous.

On the higher Homologues of Chinoline.

In his "Researches on Chinoline and its Homologues"*, the author showed that the distillate from cinchonine yielded a base above chinoline, to which he gave the name of lepidine. He also obtained a base of the same formula from coal-tar, which he subsequently showed to be isomeric and not identical with lepidine. He has recently proposed the name of iridoline† for this base. He also obtained from coal-tar a base having the formula $\text{C}^{11} \text{H}^{11} \text{N}$, to which he gave the name of cryptidine.

* Trans. Roy. Soc. Edinb. xxi. part 3. 377.

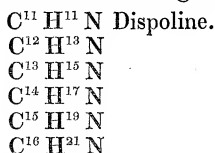
† Chem. Soc. Journ. New Ser. i. 357.

In this paper he shows that the distillate from cinchonine contains not only a base isomeric with cryptidine, and which he calls dispoline, but also several other homologues of still higher atomic weight.

The separation of these bases is very difficult. They boil at too high a temperature to allow of separation by means of fractional distillation, and, in fact, most of them distil above the range of the mercurial thermometer.

The author gives the details of the methods employed by him to purify the mixtures of bases from resinous and tarry matters; they will not, however, be quoted in this abstract.

After trial of various methods of separation, the author finally adopts fractional precipitation of the platinum-salts. By following out this method, he obtained the platinum-salts of the following bases:—



He has not given names to the homologues above dispoline.

Summary.—The author concludes from the results of the first portion of the investigation of which the above is an abstract, that the base, of the formula $\text{C}^7 \text{H}^9 \text{N}$, existing in the distillate from cinchonine, is distinct from that obtained from Dippel's oil.

He submits also that the second portion of the investigation shows the chinoline series to consist of no less than eight members, three of them being isomeric with certain bases from coal-oil.

In conclusion he calls attention to the fact that the eighth homologue of chinoline differs only by $\text{C}^4 \text{H}^4 \text{NO}^2$ from cinchonine itself, and he is of opinion that bases free from oxygen exist in the distillate from cinchonine, containing almost, if not quite, as many equivalents of carbon as the cinchona alkaloids themselves.

- V. "On the Synchronous Distribution of Temperature over the Earth's Surface." By HENRY G. HENNESSY, F.R.S., &c. Received May 26, 1864.

(Abstract.)

The results presented in the author's paper, entitled "On the Simultaneous Distribution of Heat throughout the superficial parts of the Earth" *, are confirmed and extended in the present communication.

* June 19, 1862. Proceedings, vol. xii. p. 173.